(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) **Title:** A METHOD FOR MEASURING THE CONCENTRATION OF IMPURITIES IN NITROGEN, HYDROGEN AND OXYGEN BY MEANS OF ION MOBILITY SPECTROMETRY
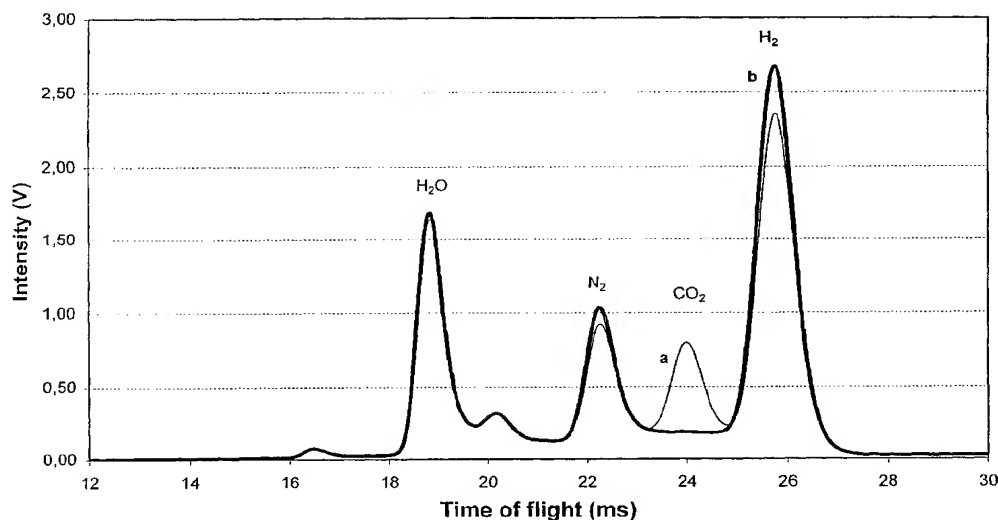
(57) **Abstract:** A method for the quantitative analysis of the impurities content in nitrogen, hydrogen and oxygen by emans of ion mobility spectrometry is described, consisting in using argon, or a mixture containing no impurities and consisting of the gas which has to be analyzed and argon, as a counterflow gas in the separation zone of the ion mobility spectrometer.

"A METHOD FOR MEASURING THE CONCENTRATION OF IMPURITIES IN NITROGEN, HYDROGEN AND OXYGEN BY MEANS OF ION MOBILITY SPECTROMETRY"

5   The present invention relates to a method for measuring the concentration of impurities in nitrogen, hydrogen and oxygen by means of ion mobility spectrometry.

Nitrogen, hydrogen and oxygen are some of the gases used as reaction media, or as the actual reagents, in the integrated circuits industry. As known, in

10   the production of these devices the purity of the reagents is of utmost importance; as a matter of fact, contaminants possibly present in the reagents or in the reaction environment can be incorporated in the solid state devices, thus altering the electrical properties thereof and giving rise to production wastes. The specifications on the purity of the gases employed in the production can vary from

15   one manufacturer to another, and depending on the particular process in which the gas is employed. Generally, a gas is considered to be acceptable for the production when its content in impurities is not higher than 10 ppb (parts per billion); preferably, the content in impurities is lower than 1 ppb. As a result, it is important to be able to measure extremely low concentrations of impurities in the

20   gases in a precise and reproducible way.

A technique which can be used for this purpose is ion mobility spectrometry, known in the field with the abbreviation IMS; the same abbreviation is used also for the instrument with which the technique is carried out, in this case indicating "Ion Mobility Spectrometer". The interest for this

25   technique derives from its very high sensibility, associated with the limited size and cost of the instrument; by operating in appropriate conditions it is possible to sense species in the gas or vapor phase in a gaseous medium in quantities of the order of the picograms (pg, that is, 10^{-12} grams), or in concentrations of the order of parts per trillion (ppt, equivalents to a molecule of analyzed substance every

30   10^{12} gas molecules of the sample). IMS instruments and methods of analysis in which they are employed are described, for example, in US patents 5,457,316 and

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5,955,886 in the name of the US company PCP Inc, and in US patent 6,229,143, in the name of the Applicant.

An IMS instrument is essentially formed of a reaction zone, a separation zone and a collector of charged particles.

In the reaction zone takes place the ionization of the sample comprising the gases or vapors to be analyzed in a carrier gas, commonly by means of beta-radiations emitted by ^{63}Ni. The ionization takes place mainly on the carrier gas with the formation of the so-called "reagent ions", whose charge is then distributed on the present species depending on their electron or proton affinities or their ionization potentials.

The reaction zone is divided from separation zone by a grid which, when kept at a suitable potential, prevents the ions produced in the reaction zone from entering into the separation zone. The moment when the grid potential is annulled, thus allowing the ions to enter into the separation zone, is the "time zero" of the analysis.

The separation zone comprises a series of electrodes which create an electric field such that the ions are carried from the reaction zone towards a collector. In this zone, which is kept at atmospheric pressure, a gas flow having opposite direction with respect to that of the ions movement is present. Commonly the counterflow gas, defined in the field as "drift gas", is an extremely pure gas corresponding to the gas whose content of impurities has to be determined; as an example, in an IMS analysis for determining the content of impurities in nitrogen, normally the drift gas is pure nitrogen. The velocity of motion of the ions depends on the electric field and on the cross-section of the same ions in the gaseous medium, so that different ions take different times for crossing the separation zone and for reaching the particle collector. The time passed from the "time zero" to the time of arrival on the particle collector is called "time of flight". The collector is connected to the signal processing system, which transforms the current values sensed as a function of time in the final graph wherein peaks corresponding to the various ions as a function of the "time of flight" are shown; from the determination of this time, knowing the test conditions it is possible to determine

the presence of the substances which are object of the analysis, whereas from the peak areas with suitable computation algorithms it is possible to calculate the concentration of the corresponding species.

In spite of its conceptual simplicity, the application of the technique involves some difficulties in the interpretation of the analysis results. This is due firstly to the fact that the net charge distribution among the various present species is the result of equilibria which depend on various factors, with the result that the peaks corresponding to one impurity can be modified in intensity, or even disappear, depending on the presence of other impurities. The book "Ion Mobility Spectrometry" by G. A. Eiceman and Z. Karpas, published in 1994 by CRC Press, can be referred to for an illustration of the (rather complex) charge transfer principles which are the base of the technique. Further, keeping constant the chemical composition of the gas, the results depend on the analysis parameters, such as the electric field applied in the separation zone, the flow rate of the gas which has to be analyzed and the flow rate of the drift gas.

As a consequence of these phenomena, the shape of the graph resulting from an IMS analysis is strongly dependent on the analysis conditions. The computation algorithms used for interpreting the analysis results are based on the deconvolution of the complete graph and on the relative measure of the areas of all the present peaks. The best results are obtained when each present ionic species gives rise to a separate peak in the graph. The analysis is still possible, although with greater difficulties, when the time of flight of a limited number of different species are similar, giving rise to a few peaks derived from the superimposition of singular peaks; in these cases it is necessary to resort to hypotheses about how the peak area is to be shared among the different species, with the risk however of introducing errors in the analysis. Finally, the IMS analysis (also the qualitative one) is impossible when large superimpositions between peaks corresponding to different species occur.

Because of the complexity of the phenomena into play, there is no standard method for applying the IMS technique, and each analysis has to be studied separately in order to define the conditions which allow to obtain a good

separation of all the peaks corresponding to the different species which can be present in the gas under analysis.

Object of the present invention is to provide a method for measuring the concentration of impurities in nitrogen, hydrogen and oxygen by means of ion mobility spectrometry.

This object is obtained according to the method of the present invention which consists in employing as the counterflow gas in the separation zone of the ion mobility spectrometer pure argon or a mixture, containing no impurities, of argon and the gas under analysis, said mixture containing at least 80% by volume of argon in case of an argon/nitrogen mixture, and at least 50% by volume of argon in case of argon/hydrogen or argon/oxygen mixtures.

In particular, with the method according to the invention the best results are obtained by using a ratio between the flow rate of argon (or the argon rich mixture) and the flow rate of the gas under analysis which is variable according to the nature of the latter.

The invention will be described in the following with reference to figures 1 to 8, which show the results of IMS analyses carried out according to the procedure of the invention and of comparative analyses, carried out in conditions not according to the invention.

The standard way to carry out an IMS analysis requires the use, as the drift gas, of the same gas (obviously pure) as the main gas in the sample whose impurity content has to be determined.

On the contrary, the inventors have found that, in the case of the analysis of impurities in nitrogen, hydrogen or oxygen, the use as drift gas of pure argon, or of suitable argon/nitrogen, argon/hydrogen or argon/oxygen mixtures containing no impurities, allows the quantitative analysis to be carried out with good and reproducible results; said suitable mixtures have been found to be an argon/nitrogen mixture containing at least 80% by volume of argon in case of the analysis of impurities in nitrogen, or argon/hydrogen or argon/oxygen mixtures containing at least 50% by volume of argon in case of the analysis of impurities in hydrogen and oxygen, respectively.

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The use of argon or of argon rich mixtures allows to obtain graphs wherein the peaks corresponding to the different species are separated, thus enabling a reliable quantitative analysis as discussed above. On the contrary, by using as drift gas the same gas whose content in impurities has to be determined, graphs with one or more superimposed peaks are generally obtained. For the sake of brevity, in the remainder of this text reference will be made to the use of argon alone as drift gas, meaning however also the above defined argon rich mixtures.

It has also been found that for the purposes of the invention it is preferable that the ratio between the flow rate of argon (drift gas) and the flow rate of the gas whose impurities content is to be determined be different according to the chemical nature of the gas under analysis. In particular, said ratio is preferably equal to at least 10 in the case of hydrogen, at least 5 in the case of nitrogen, and comprised either between 0.3 and 1.5 or between 6 and 10 in the case of oxygen. The inventors have found that, in the case of hydrogen and nitrogen, the flow rate ratios between drift gas and gas under analysis allow the best separation of the different peaks to be obtained. In the case of the oxygen, a ratio lower than 1 between the flow rate of drift gas and gas under analysis gives rise to "noises" in the signal, such as irregularities in the shape of the peaks which decrease their area (decreasing the sensibility of the analysis) and make the determination of the same area much more complex, and consequently may introduce errors in the quantitative analysis.

On the other hand, a too high ratio between the flow rate of argon and that of the gas to be analyzed has the effect of diluting the latter, with the risk of diminishing the method sensibility.

As a compromise between the opposed needs illustrated above, the ratio between the flow rate of argon and of the gas under analysis is preferably maintained at relatively low values; said ratio will be thus preferably comprised between 15 and 25 in the case of hydrogen, between 5 and 10 in the case of nitrogen and preferably of about 0.5 or about 8 in the case of oxygen.

The invention will be further illustrated by the following examples. The examples have the purpose of demonstrating how, by operating in the invention

conditions it is possible to obtain by the IMS analysis graphs which have a better peak separation with respect to the graphs obtained in condition which are not according to the invention; as above discussed, graphs with separated peaks can be more easily interpreted giving rise to more reliable analysis results. For the tests, suitable mixtures are prepared by additioning selected impurities to the base gas; in particular, carbon dioxide (CO_2) is added to hydrogen, oxygen to nitrogen and water to oxygen.

The test results are reported in graphs, showing peaks as a function of the time of flight of the corresponding ions measured in milliseconds (ms); the peaks have an area corresponding to the concentration of the different ions. These ions are generally complex species, which may comprise one, two or more molecules of the ionized gas, possibly associated to one or more molecules of the carrier gas (this phenomenon is also referred to in the field as "clustering"); for the sake of simplicity, the main peaks in the figures are identified with the formula of the molecular species to which they are ascribed instead of with the formula of the corresponding actual ion. The peak intensity is given in volts (V); the transformation of the current directly measured by the collector (number of ions which collide on the collector in the unit of time) into the value in volts reported in the graphs on the ordinate axis is operated by the instrument electronics. The ionization of the sample is carried out by a radioactive source of ^{63}Ni. The separation zone of the employed instrument is 8 cm long; in all the tests the electric field in the separation zone is equal to 128 V/cm.

EXAMPLE 1

Two IMS analyses are carried out on hydrogen samples.

A first test is carried out at 80 °C according to the preferred embodiment of the method of the invention, that is, by using argon as drift gas and a ratio of 16 between the flow rate of argon and that of the sample. As sample gas in the test it is used hydrogen to which, by means of a calibration system based on mass flowmeters, 5 ppb of nitrogen and 10 ppb of CO_2 are added as intentional impurities; this sample further contains a few ppb of water, which represent a practically ineliminabile base. The results of the test are reported in graph in

figure 1 as curve **a** (thin line in the figure). As a comparison, in the figure are also reported the results of a second test, carried out in the same conditions but on a hydrogen sample to which no CO_2 has been added (curve **b**, thick line).

EXAMPLE 2

5   The tests of example 1 are repeated, using a ratio of 8 between the flow rate of argon and that of the hydrogen sample. The results of the analysis of hydrogen containing 10 ppb of CO_2 are given in graph in figure 2 as curve **c** (thin line) whereas the results of the test carried out on hydrogen not additioned of CO_2 are given in the same figure as curve **d** (thick line).

10   ### EXAMPLE 3 (COMPARATIVE)

The tests of example 1 are repeated in conditions different from those according to the invention, that is, by employing pure hydrogen as the drift gas; the ratio between the flow rate of the drift gas and that of the sample gas is 12. Two tests are carried out, one with hydrogen containing 10 ppb of CO_2 and one

15   with hydrogen not additioned with this impurity, but the results of the two analyses are completely superimposed in the only curve reported in the graph in figure 3.

EXAMPLE 4

Two IMS analyses is carried out on nitrogen samples.

20   A first test is carried out at 110 °C according to the preferred embodiment of the method of the invention, that is, using argon as drift gas and a ratio of 5.7 between the flow rate of argon and that of the nitrogen sample. The sample gas is prepared, using the same the calibration system of example 1, adding to nitrogen 15 ppb of oxygen as an intentional impurity; in this case too the sample contains a

25   few tenths of ppb of water which cannot be eliminated. The results of this test are reported in the graph in figure 4 as curve **e** (thin line). The test is then repeated with nitrogen not additioned with O_2 and the results are given in the same figure as curve **f** (thick line).

EXAMPLE 5

30   The tests of example 4 are repeated, but using a ratio of 1 between the flow rate of argon and that of nitrogen. The results of the test with nitrogen additioned

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with O_2 are reported in the graph in figure 5 as curve **g** (thin line) whereas the results of the test carried out with nitrogen not additioned with O_2 are given in the figure as curve **h** (thick line).

EXAMPLE 6 (COMPARATIVE)

The tests of example 4 are repeated in conditions different from those according to the invention, that is, by employing pure nitrogen as drift gas; the ratio between the flow rate of the drift gas and that of the sample of gas to be analyzed is 2.5. The results of the test on nitrogen additioned with O_2 are given in the graph in figure 6 as curve **i** (thin line), whereas the results of the test carried out on nitrogen containing no O_2 are given in the same figure as curve **l** (thick line).

EXAMPLE 7

An IMS analysis is carried out on an oxygen sample. The test is carried out at 80 °C according to the preferred embodiment of the invention method, by using argon as drift gas and a ratio of 1 between the flow rate of argon and that of the oxygen sample. With the calibration system of example 1, 5 ppb of water are added to oxygen. The test results are given in a graph in figure 7.

EXAMPLE 8 (COMPARATIVE)

The test of example 7 is repeated in conditions different from those according to the invention, that is, by employing an oxygen flow containing no impurities as drift gas; the ratio between the flow rate of the drift gas and that of the gas to be analyzed is 1. The results of the test are given in graph in figure 8.

The results of analyses of impurities in hydrogen are summarized in figures 1-3. The times of flight in the various figures are different because, changing the drift/sample flow rate ratio also modified are the clustering of ions and consequently the velocities of motion of cluster ions in the separation zone.

Figure 1 refers to analyses run according to the preferred embodiment of the invention, that is, argon as drift gas and ratio between the flow rates of drift and sample in the preferred range. Curve **a** in figure 1 is relevant to the analysis of a sample of hydrogen containing CO_2 and nitrogen, whereas curve **b** is relevant to the analysis of a similar sample without CO_2. From the comparison of these two

curves is possible to determinate that the analysis carried out according to the preferred embodiment of the invention is able to reveal the different impurities as well distinct peaks, each one easily identifiable, and whose areas (correlated to the concentration of the impurity) can be easily determined.

5   Figure 2 shows two more curves; still obtained according to the invention (argon as drift gas) but in a less preferred embodiment thereof, that is, with a ratio between flow rates of drift and sample lower than 10. Again, one test is carried with hydrogen containing 10 ppb of CO_2 and 5 ppm of N_2, and the second one for hydrogen with no CO_2. From the curves obtained in these two cases (respectively

10   c and d) it is observed that in case of the sample containing only nitrogen the shape of the peak relative to this gas is less defined than in the curves in Fig. 1, and by adding one impurity, CO_2, the peaks of CO_2 and that of N_2 are superimposed; in these conditions it is still possible to carry out the analysis, but with greater difficulties in the deconvolution of the peaks and in the quantitative

15   calculation of the concentration of impurities.

Finally, fig. 3 relates to analyses carried out according to the standard modality of the prior art, that is, using hydrogen as drift gas. As it is easily observed, this way of operating leads to a spectrum essentially formed of one single peak, wherein it is impossible to recognize the presence of different

20   species; obviously, in these conditions both the qualitative and the quantitative analyses of the different impurities are impossible.

In the analysis of nitrogen too (figs. 4-6), the use of argon as drift gas allows to obtain a spectrum having separated peaks.

Figure 4 relates to analyses carried out according to the preferred

25   embodiment of. the invention, that is, with a ratio between the flow rate of drift gas and sample higher than 5. Curves e and f respectively show the analysis of a nitrogen sample containing O_2 as intentionally added impurity and of a sample containing no O_2; also in this case peaks are present which can be ascribed to water present as an ineliminabile base in concentration of few ppb. As it can be

30   noted, the peak for the impurity O_2 in curve e is well isolated and defined, thus allowing an easy determination of the concentration of this impurity.

Figure 5 refer to analyses carried out by still operating according to the invention (argon drift) but in a less preferred embodiment thereof (ratio between flow rate of drift and of sample lower than 5), the peaks of oxygen and water are superimposed; it is still possible to determinate the quantity of oxygen, but in this case as a difference with respect to the quantity of water (whose concentration can be measured from the peak at about 23 ms).

The curves in fig. 6 are obtained by operating according to the method of the prior art, that is by using pure nitrogen as drift gas. Curves i and l, relevant respectively to nitrogen containing O_2 and nitrogen containing no O_2, are almost completely superimposed and present a smaller number of peaks; in these conditions it is not possible to correctly evaluate the area of the oxygen peak, and the analysis of this impurity is practically impossible.

Finally, figures 7 and 8 are relative to analyses of traces of water in an oxygen sample according respectively to the invention and to the prior art. The graph reported in figure 7 (use of argon as drift gas, according to the invention) shows two neat and rather well separated peaks; on the other hand, the graph of figure 8 (use of oxygen as drift gas, prior art) shows, in the zone between 19 and 23 ms, a series of spurious signals which complicate the deconvolution of the graph introducing a possible source of errors in the quantitative analysis.

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CLAIMS

1. A method for measuring the concentration of impurities in nitrogen, hydrogen and oxygen by means of ion mobility spectrometry consisting in employing as the counterflow gas in the separation zone of the ion mobility spectrometer pure argon or a mixture of argon and the gas that is the carrier in the sample under analysis, said mixture containing no impurities and containing at least 80% by volume of argon in case of an argon/nitrogen mixture, and at least 50% by volume of argon in case of argon/hydrogen or argon/oxygen mixtures.

2. A method according to claim 1, wherein the gas which is to be analyzed is hydrogen and the ratio between the flow rate of argon or mixture of argon and the flow rate of hydrogen is equal to or higher than 10.

3. A method according to claim 2, wherein said ratio is between 15 and 25.

4. A method according to claim 1, wherein the gas to be analyzed is nitrogen and the ratio between the flow rate of argon or mixture of argon and the flow rate of nitrogen is equal to or higher than 5.

5. A method according to claim 4, wherein said ratio is between 5 and 10.

6. A method according to claim 1, wherein the gas which has to be analyzed is oxygen and the ratio between the flow rate of argon or mixture of argon and the flow rate of oxygen is comprised either between 0.3 and 1.5 or between 6 and 10.

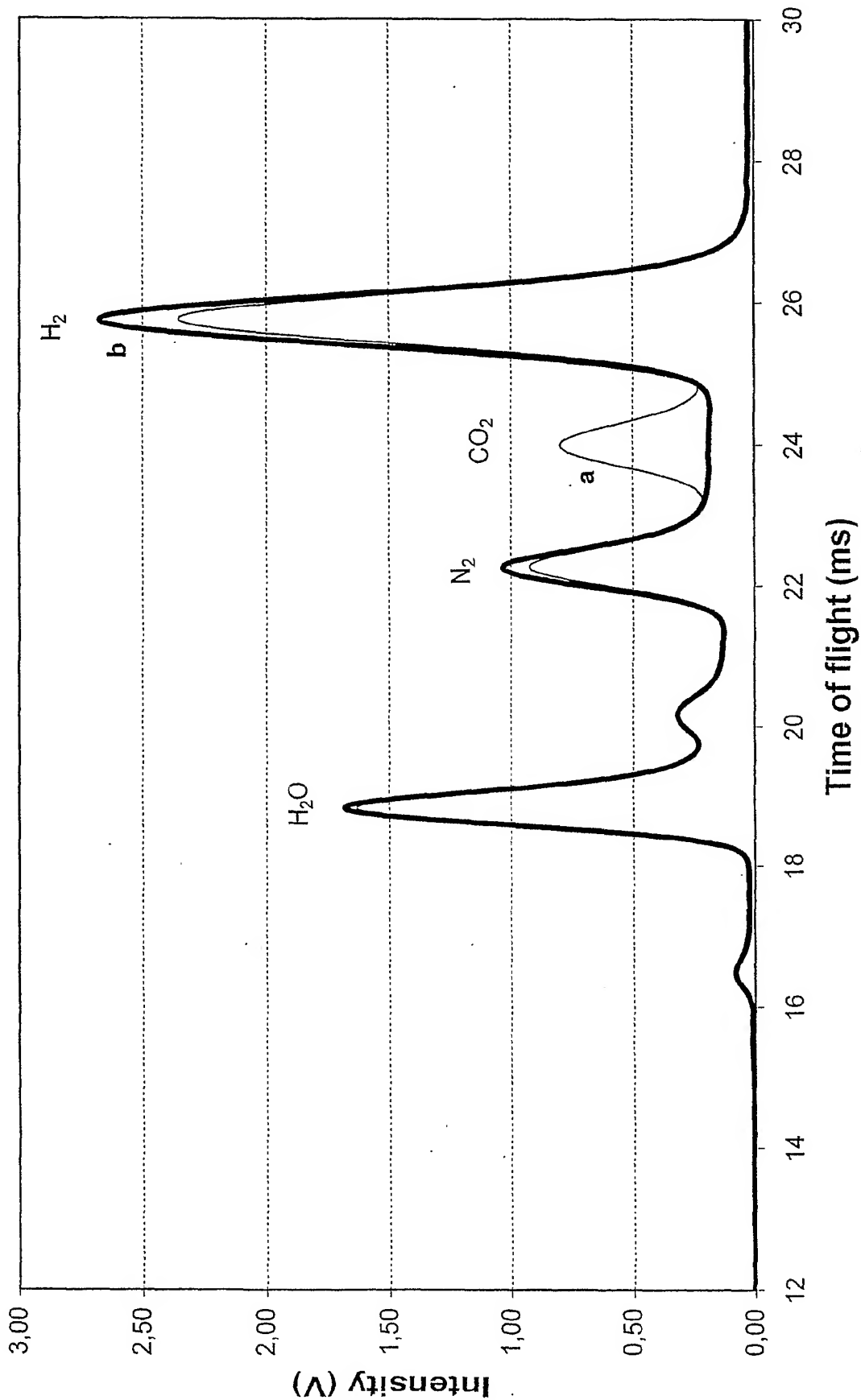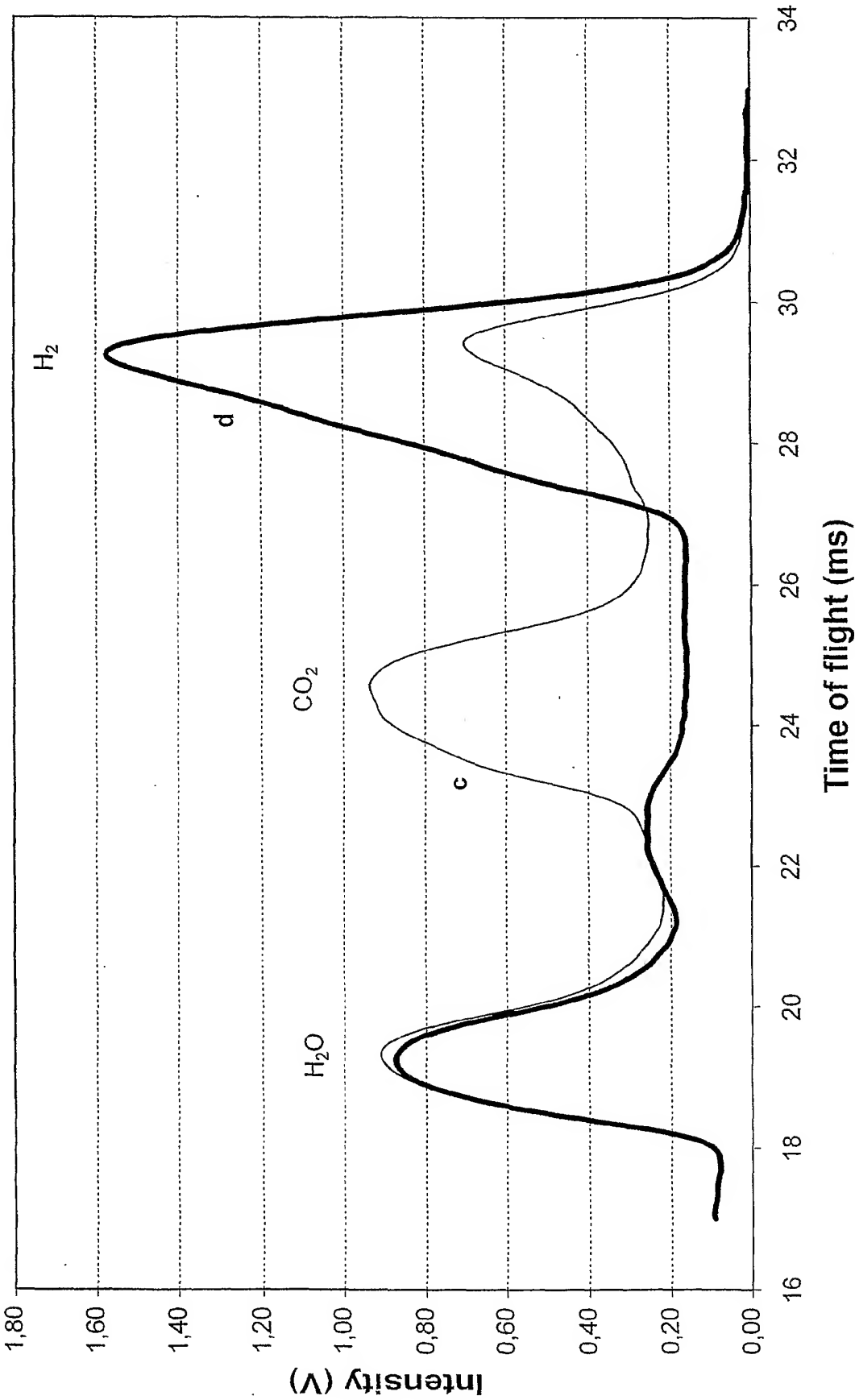7. A method according to claim 6, wherein said ratio is equal to about 0.5 or 8.
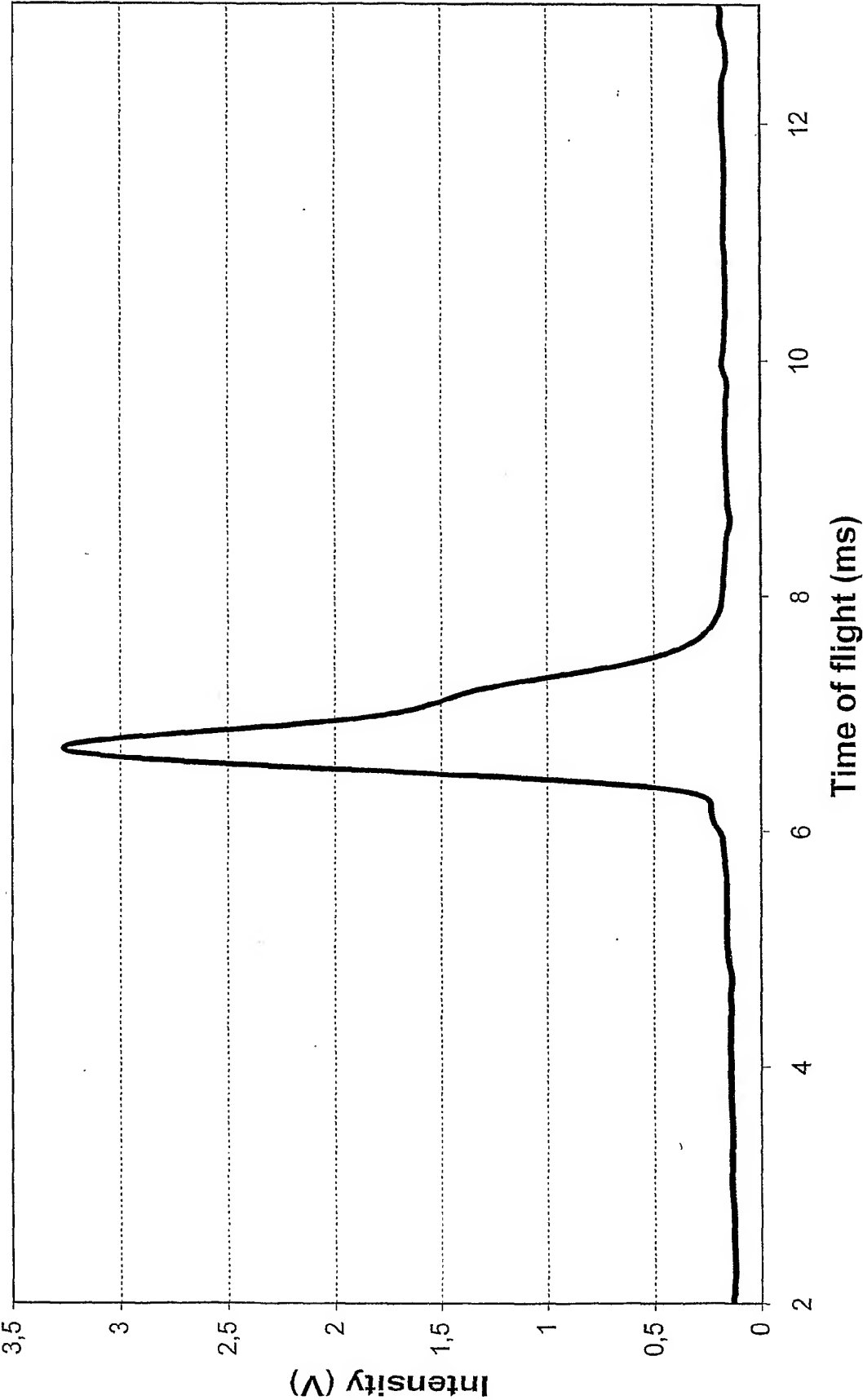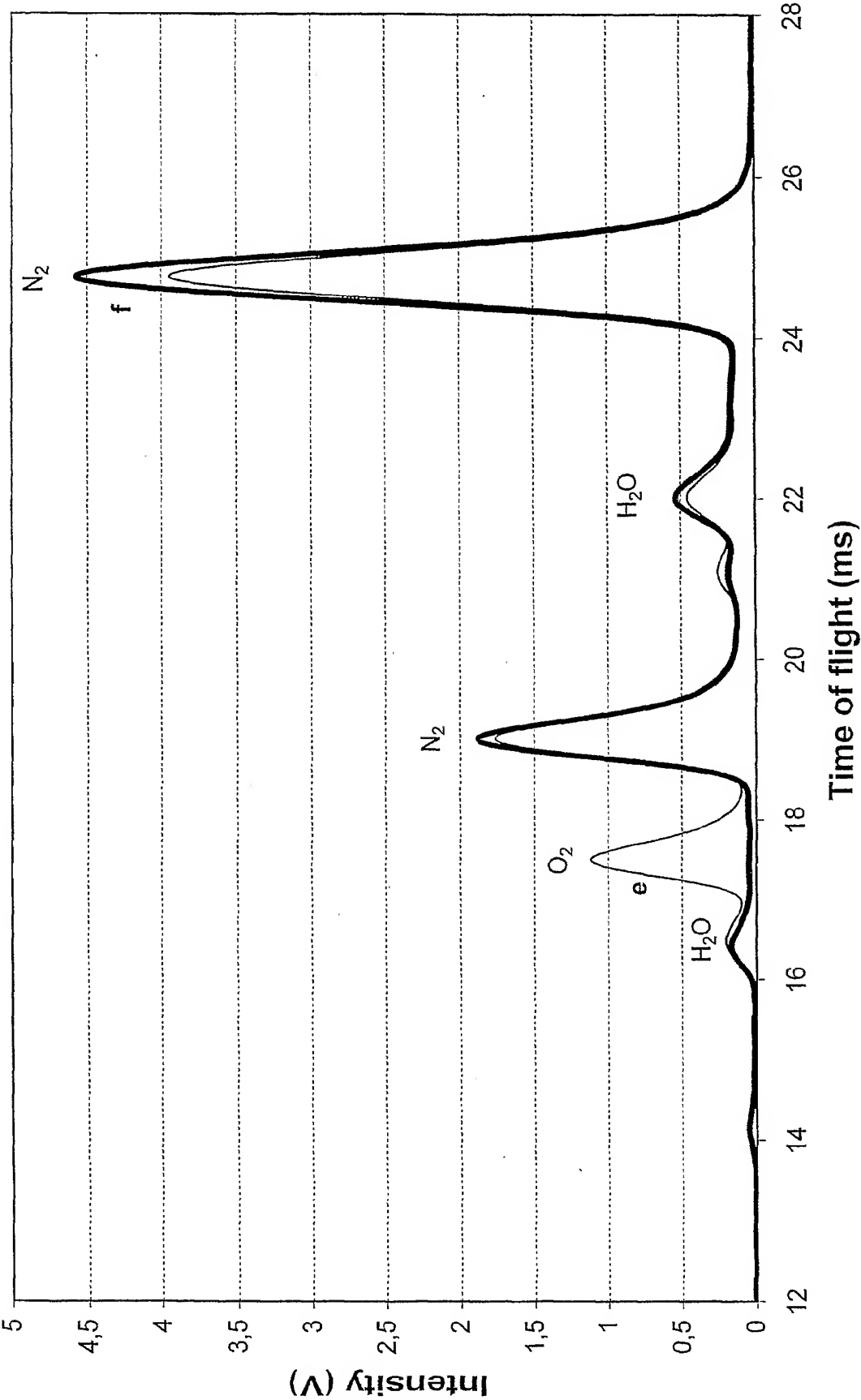
Fig. 1

Fig. 2

Fig. 3

Fig. 4
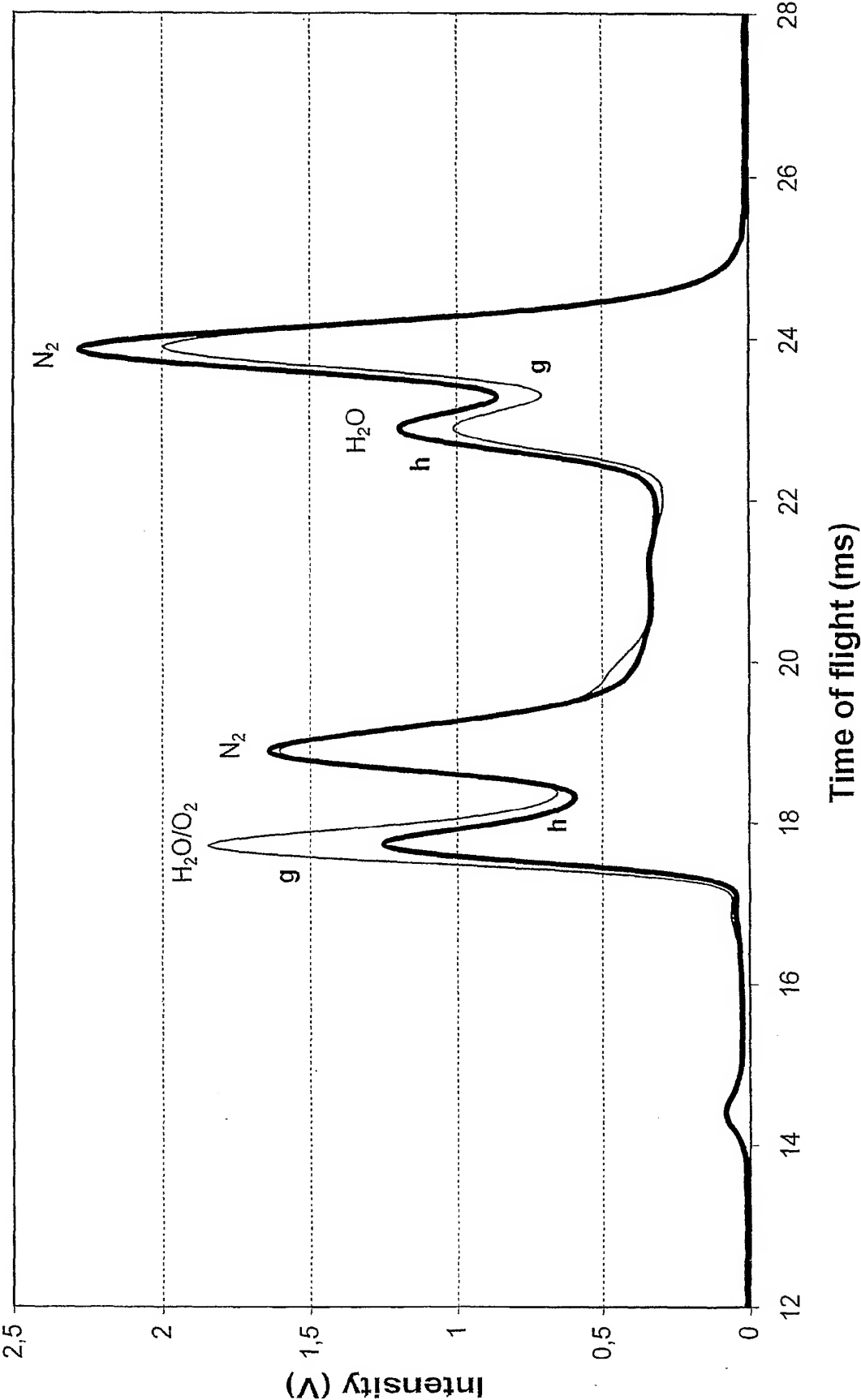
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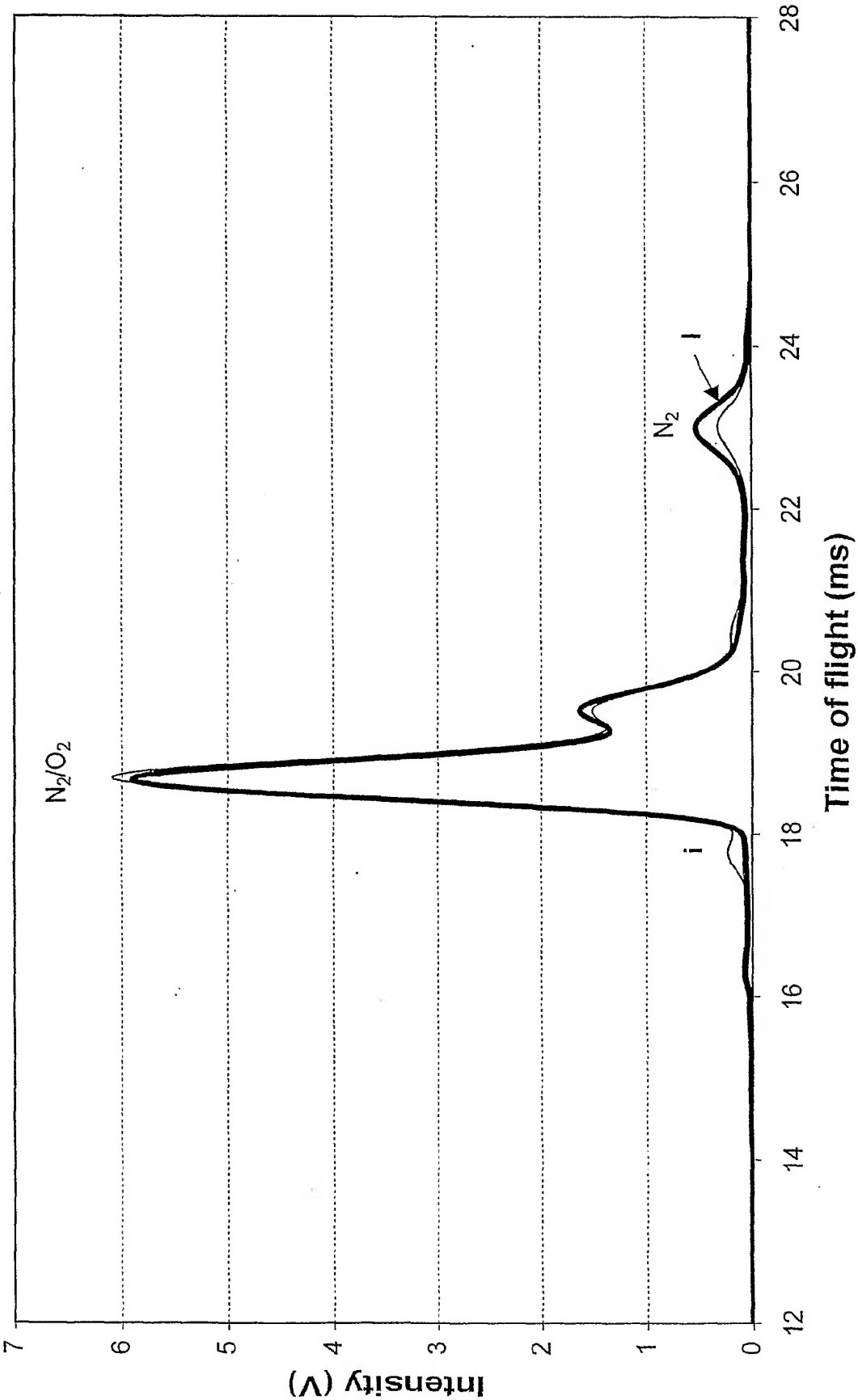
Fig. 6
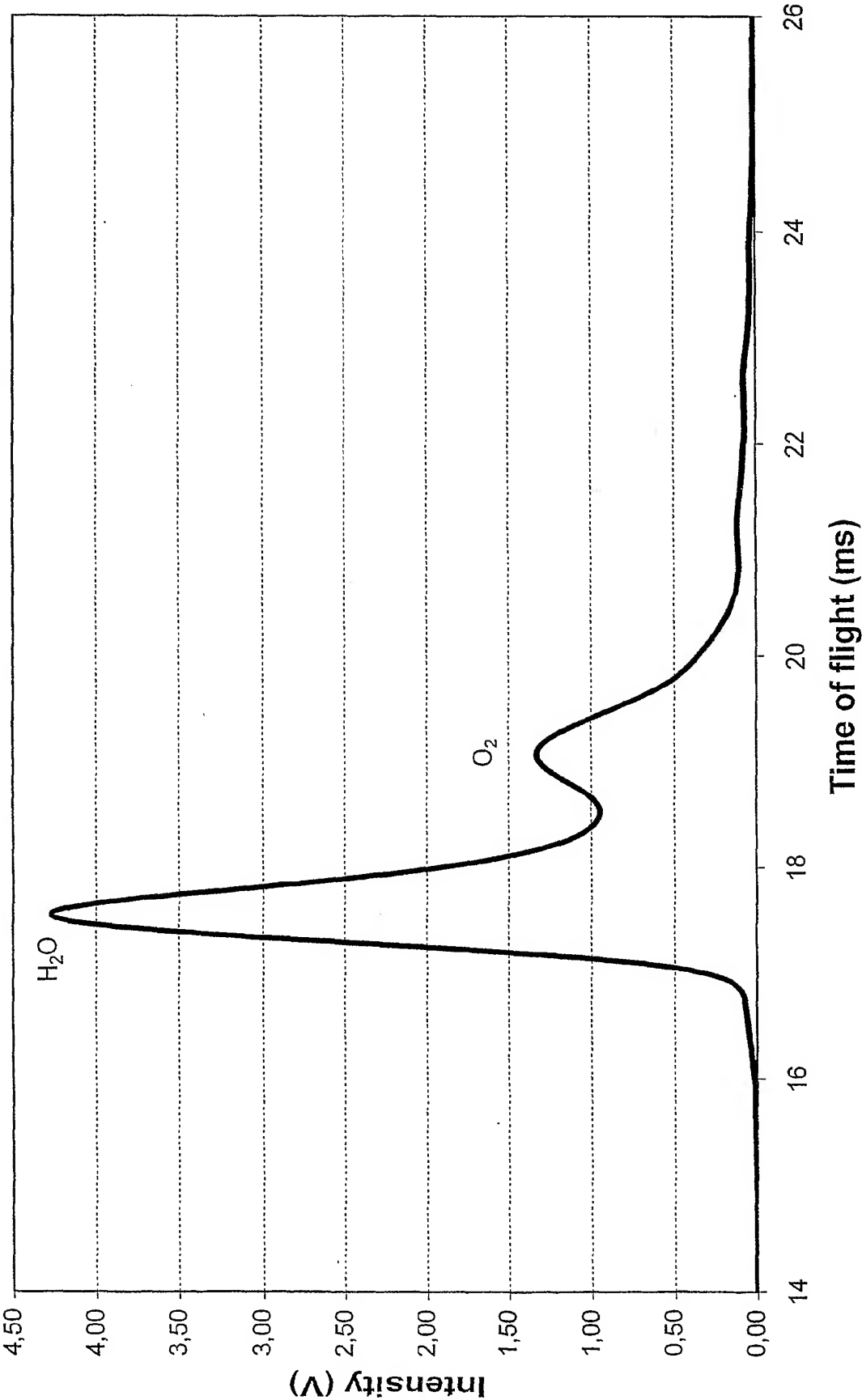
Fig. 7
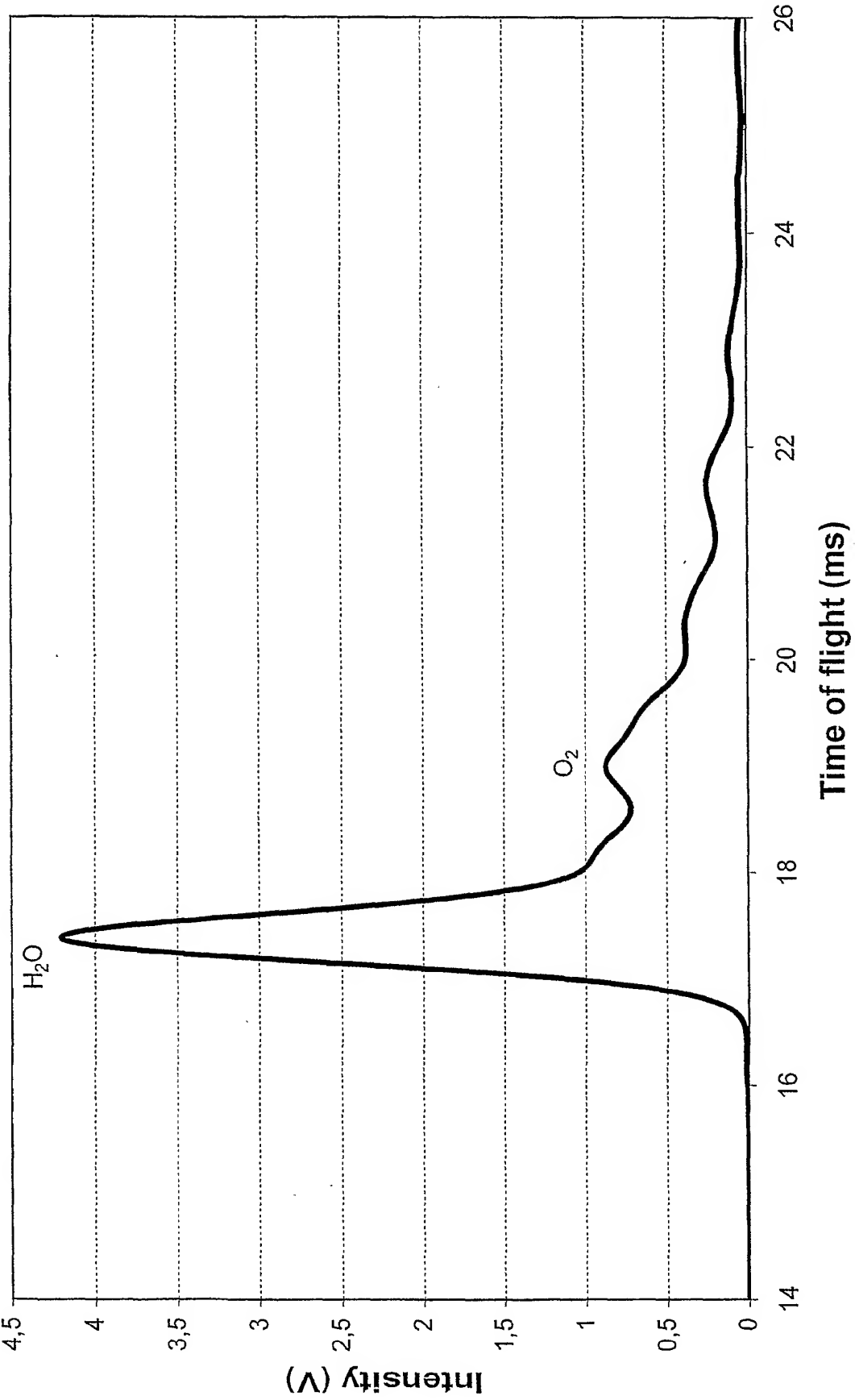
Fig. 8

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   G01N27/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, COMPENDEX, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 52432 A (MASSACHUSETTS INST TECHNOLOGY) 8 September 2000 (2000-09-08)	1
A	page 14, line 14 – line 18 page 16, line 17 – line 21	2-7
X,P	EP 1 154 268 A (AIR PROD & CHEM) 14 November 2001 (2001-11-14)	1
A,P	paragraph '0013! paragraph '0021! – paragraph '0023! paragraph '0025! paragraph '0033! paragraph '0037! – paragraph '0038! figures 3,4	2-7
A	US 5 457 316 A (COHEN MARTIN J ET AL) 10 October 1995 (1995-10-10) cited in the application the whole document	1-7

☐ Further documents are listed in the continuation of box C. ☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search	Date of mailing of the international search report
22 March 2002	04/04/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Stussi, E

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0052432	A	08-09-2000	WO US	0052432 A2 6239428 B1	08-09-2000 29-05-2001
EP 1154268	A	14-11-2001	EP	1154268 A2	14-11-2001
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